ULTRAMICROPOROUS MEMBRANES FOR HYDROGEN SEPARATION

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SUMMARY: Fuel cell systems offer excellent efficiencies when compared to internal combustion engines, which result in reduced fuel consumption and greenhouse gas emissions. One of the areas requiring research for the success of fuel cell technology is the H_2 fuel purification to reduce CO, which is a poison to fuel cells. Molecular sieve silica (MSS) membranes have a potential application in this area. In this work showed activated transport, a characteristic of ultramicroporous (dp<5Å) materials in which the permeation increased with temperature. H_2 permeance resulted in 1.2 x 10^{-8} mol.m^{-2}.s^{-1}.Pa^{-1} and a H_2/CO permselectivity of 33 (200^{o}C, 2 bar □P). Observations made during surface preparation showed that the permeance was not hindered by the intermediate layers, and that only the top (selective) layer played a significant role in reducing gas permeance. The pressure difference across the membrane showed that the permeance was pressure independent, except at pressures below 2 bar, which resulted in a higher permeance. High quality membranes purified a mixed gas containing 42% H_2 by over two fold with the remainder being made up of N_2, CO_2 and CO. These are encouraging results for applying MSS membranes to environmentally promising fuel cell systems.

1. INTRODUCTION

Highly populated urban areas are exposed to pollution arising from transport systems. Today, modern internal combustion engine (ICE) vehicles equipped with catalytic converters essentially eliminate toxic emissions such as CO and NO_x, however CO_2 is still a by-product. It is now commonly accepted that CO_2 is a greenhouse gas and must be reduced to prevent global warming. Fuel cell systems incorporating high quality membranes can offer a solution to this. Other major factors driving membrane technology in fuel cell systems are regulations, energy efficiency and cost effectiveness. Fuel cells emit less carbon dioxide and nitrogen oxides per kilowatt of power generated (ECW, 2000). As processes become more efficient by employing membranes, they greatly reduce energy consumption leading to lower usage of fossil fuels and lower emission of greenhouse gases. Low temperature fuel cells with membranes for H_2 removal from CO have electrical efficiency of 42% (Rastler et al., 1996), which is much higher than the conventional combustion engines efficiency of up to 33%.

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The fuel used by common fuel cells is H_2, and has the distinct advantage over other gases present in a H_2 rich stream, in that it is the smallest molecule. Impurities such as CO, formed as a by-product during H_2 production (reforming), must be removed to meet the requirement of the fuel cell. MSS membranes allow gases below a certain molecular size to permeate through and larger molecules to pass over (molecular sieving). Alternatively, metallic membranes have the best capabilities to selectively remove H_2 from gas mixtures and have attracted the attention of several research groups (Ledjeff-Hey et al.,1998; Koros and Mahajan, 2000; Lin and Rei, 2000; Tosti et al., 2000). Metallic membranes, such as Pd/Ag membranes, can offer perfect selectivity but are expensive, may not be resistant to CO and gases containing sulphur, and are reliant on expensive rare earth materials which can be dangerous and toxic to the environment if handled or disposed incorrectly. On the other hand, MSS membrane technology provides separation of H_2 from other gases, is economically feasible and made mostly of silicon, which is abundant and precursors safer to handle. Figure 1 show the application of MSS membrane technology in fuel cell fuel processing systems.

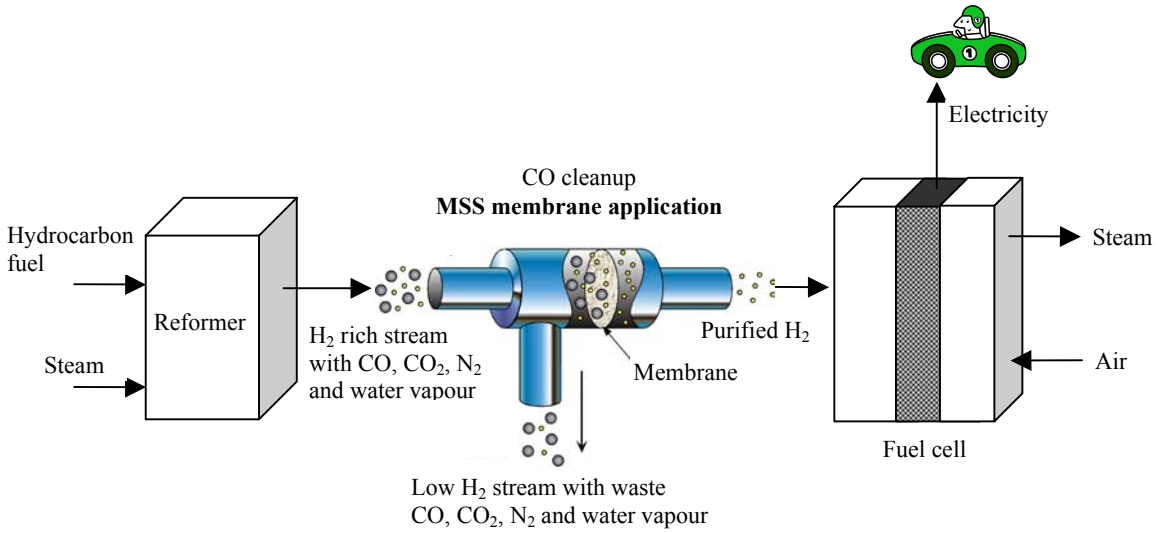

Figure 1 - Fuel cell fuel processing system showing application of MSS membrane for CO removal.

Some groups have looked at MSS membranes formed by the sol-gel process for gas separation with particular attention to separating H_2 from CO (de Vos and Verweij, 1998 and Hasegawa et al., 2002). Results for H_2 permeance and H_2/CO permselectivity (the ratio of pure H_2 and CO permeance) from these groups are presented in Table 1. These results are not consistent and vary according to the adopted synthesis techniques. This shows there is no obvious performance limit and superior membranes can be made by careful examination of reported techniques. More work must be performed to determine where improvements in MSS membrane technology can be made and to improve their consistency.

Table 1 - H_2 and CO permeation in ultramicroporous membranes at 200°C.

H_2 Permeance ($\times 10^{-8}$ mol.m^{-2}.s^{-1}.Pa^{-1})	Single gas H_2/CO permselectivity	Reference
20	126	Hasegawa et al. (2002)
174	33	de Vos and Verweij (1998)

In this work, the evolution of film formation by analysing flux permeation and H_2 selectivity towards He, CO_2, N_2 and CO is explored. This analysis is carried out at each stage of film formation as there is a sequential reduction of pore sizes from first layer to the final top selective layer. These are features of key technological importance to improve membrane performance. Also addressed is the ultramicroporous membrane capability to operate using single gases at various regimes of pressure and temperature. Single gas tests will be validated with mixed gas tests to determine if MSS membrane technology is suitable for H_2 purification in fuel cell systems.

3. PROCEDURE

The sol-gel and membrane synthesis used in this work are presented in Table 2 and described elsewhere (Diniz da Costa et al., 2002). The □-alumina substrate, (porosity 0.3, pore size 0.5-1 □m, supplied by Rojan Ceramics, Australia) was prepared by polishing with in two stages to achieve the smoothest surface by mechanical methods. The silicon sources used were tetraethylorthosilicate (TEOS) and methyltriethoxysilane (MTES). MTES contains a covalently bonded methyl group which is used to template the sol-gel. Bulk samples for characterisation were gelled at 50°C in a temperature controlled oven. Once dried, gels were calcined identically to the membrane calcination procedures to form xerogels. Pore geometry of xerogel samples was determined by N_2 adsorption using a Quantachrome Autosorb 1C-LP.

Table 2 - Sol gel preparation summary

Sol code	Alkoxide source	Synthesis description
A1	Al from Locron (Clariant GmbH, Germany)	Heat treated
T1	TEOS and MTES (Sigma Aldrich)	Acid catalysed two-step sol gel process
S1	TEOS (Sigma Aldrich)	Acid catalysed single-step sol gel process
S2	TEOS (Sigma Aldrich)	Acid catalysed two-step sol gel process

Between each coat, the membranes were calcined in a temperature ramped furnace to cast the films onto the surface. Each coating/calcination stage was repeated to repair defects. Membranes were taken out after each coat to develop a flux evolution profile. Permeance was tested in two modes. The first mode utilised a dead end permeation to enable accurate and fast testing the single gases He, H_2, N_2, CO and CO_2 at a range of temperatures and pressure differences across membrane. A mixed gas having the H_2:N_2:CO:CO_2 composition of 42.3:36.1:9.2:12.4 was also used in this mode.

The second mode was a semi-continuous setup using the mixed gas only to determine separation of gases. As the permeance of gas through the membrane was too small, no sweep gas was used. Instead, the permeate side of the membrane was purged with He and several readings made using a Shimadzu GC-17A GC until the composition at steady state was found. The retentate side of the membrane had no flow passing over. A simplified schematic of both modes is depicted in Figure 2.

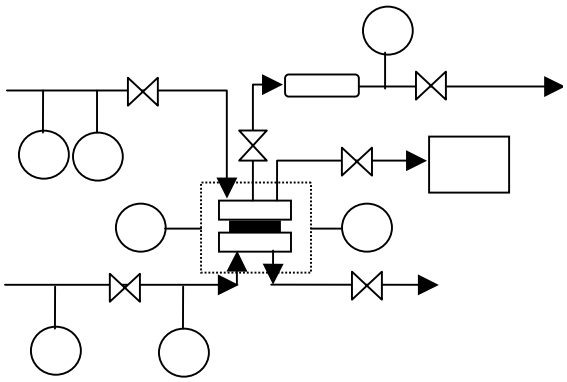

Figure 2 - Simplified schematic of mode 1 and mode 2 membrane testing systems

4. RESULTS AND DISCUSSION

Results from pore geometry measurements of xerogel samples using N_2 adsorption are listed in Table 3. The micropore characteristics determined by t-method analysis are separated from the bulk values determined from multi-BET analysis. Cylindrical pores were assumed to estimate the pore radius. Samples S1 and S2 are microporous (dp<20 Å) whilst A1 and T1 are mesoporous (20<dp<500 Å). It is observed a gradual pore size reduction from the aluminium oxide samples A1 (38Å) to the silica samples around 12-13 Å. These results follow suit the membrane synthesis strategy, as the first layer to be cast on porous supports is sol A1, and then followed sequentially by T1, S1 and S2. It is important to note here that the values for pore size are purely qualitative as thin films produce much smaller pores than bulk xerogel due to fast evaporation and gellation times.

Table 3 - Pore geometry of xerogel samples using N_2 adsorption

Sample	Micropore surface area ($m^2.g^{-1}$)	Micropore volume ($cm^3.g^{-1}$)	Average micropore radius (Å)	Total BET surface area ($m^2.g^{-1}$)	Total pore volume ($cm^3.g^{-1}$)	Average pore radius (Å)
A1				121	0.229	38
T1				1700	2.02	24
S1	237	0.127	10.7	251	0.146	12
S2	281	0.151	10.7	315	0.2	13

Figure 3 shows how the H_2 permeance of ultramicroporous membranes changed with each layering stage. A relatively small change was observed after coating with the primary layer (sol A1). Permeance then decreased by roughly one order of magnitude per stage until the single step coating (S1). After deposition of the two-step coat (S2), the permeance decreased by two fold. The membrane layers were than sanded to observe the extent of substrate blocking (sol soaking into substrate). After light sanding, the permeance returned to roughly that of the intermediate (T1) stage membrane. This showed that thin films formed on the surface and were responsible for flux and separation performance of the membrane.

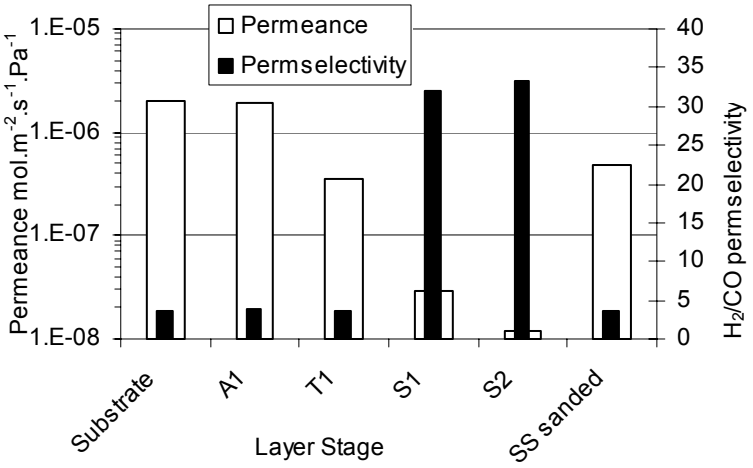

Figure 3 - Permeance evolution on membranes with layer stage (T = 200°C, □P = 2 bar)

Figure 3 also shows the single gas H_2/CO permselectivity progression with each coating stage. The permselectivity remained below the Knudsen ideal permselectivity of 3.7 until the first microporous layer (sol S1) was deposited which resulted in a permselectivity above 30. The subsequent deposition of the S2 layer did improve the permselectivity slightly, but permeance decreased by two fold indicating that the extra S2 layer was not worthwhile. This is consistent with pore geometry measurements as pore size of xerogel samples S1 and S2 were very similar. Hence, the extra S2 layer just caused an increase but in thickness resulting in lower permeation. After light sanding, the permselectivity returned to the Knudsen ideal permselectivity, showing that the substrate was not impeding permeation.

Results in Figure 4a show the effect of pressure difference across the membrane on permeance. At very small pressures (0.04 bar), permeances for the gases of study were quite similar. In this case, there was no major driving force for diffusion due to extremely low pressures as permeation of gases was almost non-existent. However, the permeation was independent of pressure difference for pressures in excess of 1-2 bar. Figure 4b shows that permeation increases with temperature, indicating the transport of molecules through the membrane was activated. It was also observed that the permeation of molecules with small kinetic diameter (He and H_2) was one to two orders of magnitude higher than the high kinetic diameter gases (CO_2, N_2 and CO). These results suggest that ultramicroporous membranes have good separation capabilities.

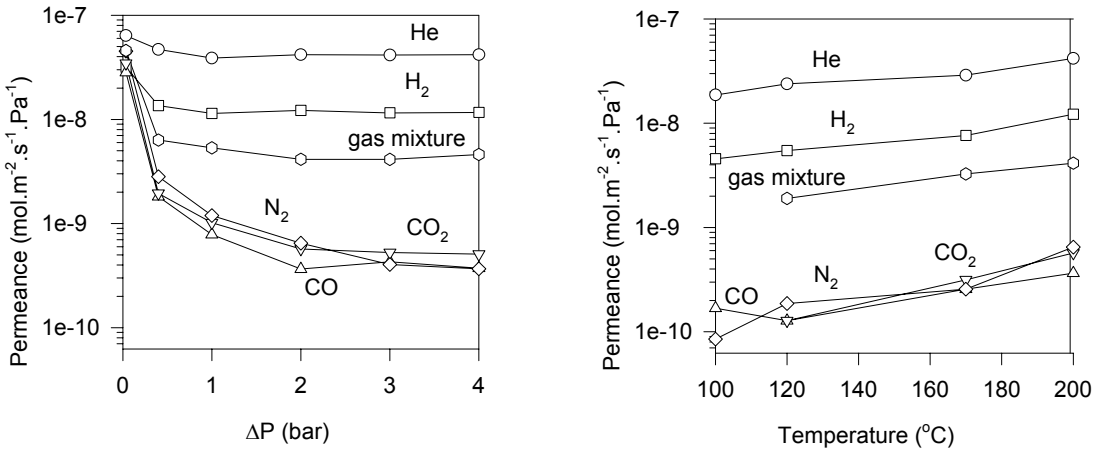

Figure 4 - Permeance as a function of (a - left) pressure difference (T = 200°C) and (b - right) temperature (□P = 2 bar)

Single gas H_2 permselectivities, permeate/retentate compositions and mixed gas H_2 selectivities are listed in Table 4. The membrane proved to selectively permeate H_2 over other gases in single and mixed gas experiments. The H_2/CO permselectivity and selectivity of 33 and 72 respectively, suggest that ultramicroporous membranes are ideal candidate for H_2 purification systems. In the latter case, a mixed gas feed stream containing 42% H_2 was filtered to a 92% H_2 purity in the permeate stream (i.e. across the membrane). The CO concentration in the permeate stream for our measurements were below the GC's 1% minimum detectable level. Hence, it should have been conservatively determined at 1% suggesting that H_2/CO selectivity of 72 in gas mixtures should be higher.

Table 4 - Single permselectivities and mixed gas selectivities (T = 150°C)

Gas	Single gas (□P = 2 bar)	Mixed gas (□P = 3 bar)		
	H_2 permselectivity	Retentate %	Permeate %	H_2 selectivity
H_2	1	42.3	91.7	1
CO_2	32	12.4	2.0	14
N_2	29	36.1	6.1	13
CO	33	9.2	0.3	72.0

5. CONCLUSIONS

Membranes, which showed high permeability of H_2 over CO_2, N_2 and CO where successfully produced. The order of single gas permeance was directly related to the physical size of the gas molecule as transport was activated (increased with temperature). The good separation of single gases allowed testing to be moved to gas mixtures. Mixed gas results showed that H_2 is greatly

purified and eliminates suspicions of transport exclusion due to the presence of more highly adsorbing gases such as CO_2. Both single gas and mixed gas permeation experiments showed that the layers responsible for selective transport of gases must be ultramicroporous due to their high H_2 flux to other gases. This work also showed that the supports and intermediate layers did not restrict the permeance and permselectivity of gases, which is mainly attributable to the top layers. The results in this work strongly suggest that MSS membranes are suitable for H_2 purification in fuel cell systems with potential application directed towards zero emission vehicles.

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